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(54) **Powder coating composition containing low temperature curable epoxy resin**

(57) The present invention relates to a powder coating composition containing a low temperature curable epoxy resin, and more particularly to a powder coating composition containing a low temperature curable epoxy resin, which can be readily cured at a low temperature, thereby capable of being applied to coating objects that are noneconomical in terms of workability

at an elevated temperature, or are thermally sensitive. The present invention provides a powder coating composition comprising 100 parts by weight of a low temperature curable epoxy resin; and 30 to 500 parts by weight of curing agent.

EP 1 323 759 A1

Description**BACKGROUND OF THE INVENTION****Field of the Invention**

[0001] The present invention relates to a powder coating composition containing a low temperature curable epoxy resin, and more particularly to a powder coating composition containing a low temperature curable epoxy resin, which can be readily cured at a low temperature, thereby capable of being applied to coating objects that are difficult in elevating temperature, or are thermally sensitive.

Description of the Related Art

[0002] Epoxy resin is a molecule having two or more epoxy functional groups. Epoxy resin is a kind of thermosetting resin irreversibly crosslinked to form a three-dimensional structure at room temperature or under the influence of heat. However, epoxy resins are different from other thermosetting resins in that curing is not carried out on heating in the absence of a catalyst or a curing agent. An epoxy resin is widely used in molded products, cast products, coatings and the like due to its excellent adhesion, mechanical property, electrical property, chemical resistance, etc.

[0003] In particular, the epoxy resin is excellent in adhesion, water resistance, and chemical resistance to various types of coating objects, including metals. Accordingly, the epoxy resin based coatings are widely used instead of alkyd resin or phenolic resin based coatings.

[0004] A powder coating composition is a coating film forming composition in the form of powder and does not use a volatile solvent such as an organic solvent or water. The powder coating composition is applied to a coating object and then heat-melted. The powder coating composition has advantages in that it does not use a solvent, can form a thick coating film with just one coating, and can use a high molecular weight resin which is not dissolved in a solvent, compared with a solvent-type coating composition. Accordingly, use and demand for the powder coating composition are increasing in fields of construction materials, automobile parts, pipes, mechanical parts, electronic products, iron furniture and the like.

[0005] The powder coating composition is generally produced as follows: a resin for a powder coating composition, a curing agent, a pigment and an additive, and the like are mixed in a blender. The mixture is placed into an extruder or a roll-mill, where it is heated at a temperature in a range of 80 to 130°C, melt-mixed and ground into a powder. Thereafter, a coating object is coated with the ground powder coating composition. Alternatively, the powder coating composition can be produced by mixing the above components in a mixer such as a ball-mill or a ribbon blender at room temperature.

[0006] The powder coating composition can be coated by various coating techniques, for example, a spray coating technique, a flow coating technique or an electrostatic coating technique. The electrostatic coating technique is most widely used.

[0007] Examples of the resin for the powder coating composition are an epoxy resin and a polyester resin. The epoxy resin is generally a bisphenol-A epoxy resin manufactured by reacting bisphenol-A and epichlorohydrin in the presence of a base or an acid. The bisphenol-A epoxy resin is excellent in chemical resistance and corrosion resistance. However, because it is cured at a high temperature, for thick metallic coating objects that cannot reach an elevated temperature within a short time, a large amount of heat energy must be applied thereto, and thus energy use increases. Further, it is difficult to apply to coating objects that are thermally sensitive.

[0008] On the other hand, in glycidyl ethers of conventional bisphenol compounds, there have been a number of suggestions that multifunctional bisphenol epoxy resins obtained by further reacting secondary hydroxyl groups of the glycidyl ethers with epichlorohydrin can be used as sealing materials, laminates of electrical and electronic components, etc (see, U.S. Pat. No. 4,623,701, Japanese Patent Laid-open Nos. Hei 5-5020, 6-248055, 6-298904, etc.). However, these references fail to disclose the manufacture of powder coating using the epoxy resins.

SUMMARY OF THE INVENTION

[0009] Therefore, the present invention has been made in view of the above problems, and it is an object of the present invention to provide a powder coating composition containing a low temperature curable epoxy resin with corrosion resistance.

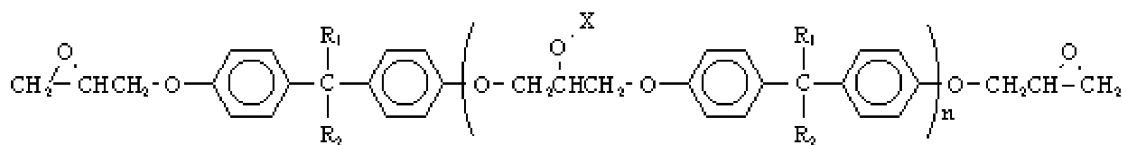
DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010] In accordance with the present invention, the above and other objects can be accomplished by the provision

of a powder coating composition comprising :

- 100 parts by weight of a low temperature curable epoxy resin represented by Formula 1 below :

Formula 1



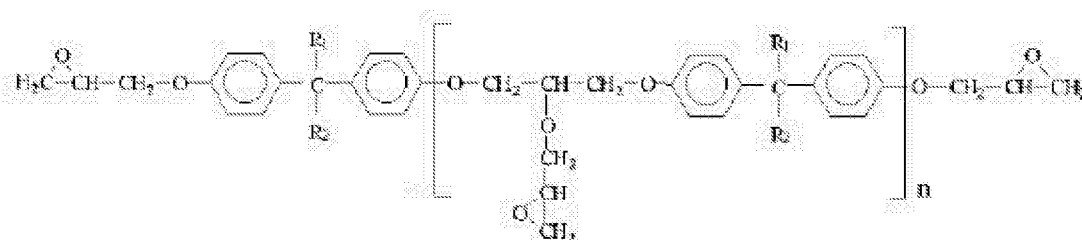
wherein :

- n is a real number of from 0.1 to 30 ;
- R₁ and R₂ are, independently, a hydrogen atom, or an unsubstituted or substituted alkyl or alkoxy group having from 1 to 5 carbon atoms ; and
- X is a hydrogen atom or glycidyl group, wherein more than 20% of X are glycidyl groups ; and

- 30 to 500 parts by weight of a curing agent.

[0011] In accordance with one embodiment, the epoxy resin is represented by Formula 4 below:

Formula 4



wherein R₁, R₂ and n are as described above.

[0012] It is preferred that R₁ and R₂ each are individually a hydrogen or a methyl group, and n is a real number of 1 to 15 ; n may also be an integer of 1 to 15.

[0013] In accordance with one embodiment of the present invention, the curing agent is preferably a phenolic curing agent such as a bisphenol-A curing agent or a polyester-based curing agent.

[0014] In accordance with another embodiment of the present invention, the powder coating composition preferably further comprises 10 to 200 parts by weight of a universal bisphenol-A epoxy resin for powder coating compositions (epoxy equivalent weight: 600 to 1500 g/eq) per 100 parts by weight of the low temperature curable epoxy resin of the Formula 1.

[0015] In accordance with yet another embodiment of the present invention, the powder coating composition preferably further comprises one or more components selected from the group consisting of a pigment, an antioxidant, a filler, a light stabilizer, a curing promoter and an ultraviolet absorber.

[0016] Examples of the alkyl group having from 1 to 5 carbon atoms, represented as "R" in formula 1, include methyl, ethyl, propyl, butyl groups, etc. n is a number of from 0.1 to 30, and preferably from 1 to 15. X is a hydrogen atom or a glycidyl group. More than 20% of X are glycidyl groups, and preferably more than 25% are glycidyl groups.

[0017] Herein, n and X refer to average values. When n is less than 0.1, or less than 20% of X are glycidyl groups in the epoxy resin, the content of multifunctional epoxy compounds not less than trifunctional is low and thus the epoxy resin is unsatisfactory in its curability and properties of the coated object.

[0018] Hereinafter, the present invention will be described in more detail.

[0019] A conventional epoxy resin is excellent in corrosion resistance but is generally cured at a high temperature.

[0031] The multifunctional low temperature curable epoxy resin of the Formula 1 used in the present invention can be prepared by polymerizing a bisphenol-A epoxy resin of Formula 2 below, and an epichlorohydrin.

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[0038] Examples of the phase-transfer catalysts include tetramethylammonium chloride, tetrabutylammonium bromide, methyltriocylammonium chloride, methyltridecylammonium chloride, N,N-dimethylpyrrolidinium chloride, N-ethyl-N-methylpyrrolidinium iodide, N-butyl-N-methylpyrrolidinium bromide, N-benzyl-N-methylpyrrolidinium chloride, N-ethyl-N-methylpyrrolidinium bromide, N-butyl-N-methylmorphonium bromide, N-butyl-N-methylmorphonium iodide, N-allyl-N-methylmorphonium bromide, N-methyl-N-benzylpiperidinium chloride, N-methyl-N-benzylpiperidinium bromide, N,

N-dimethylpiperidium iodide, N-methyl-N-ethylpiperidium acetate, N-methyl-N-ethylpiperidium iodide, etc., and tetramethylammonium chloride is more preferable.

[0039] The amount of epichlorohydrin used in the reaction is not less than 1 equivalent weight, and preferably within the range of 2~10 equivalent weight, relative to 1 equivalent weight of hydroxyl group of diglycidyl ether. The amount of the alkali compounds used in the reaction is within the range of 0.1~2.0 moles, and preferably 0.3~1.5 moles, relative to 1 equivalent weight of glycidylated hydroxyl group. The amount of the phase-transfer catalysts used is within the range of 0.01~10 mol%, and preferably 0.2~2 mol%, based on the total weight of the reactants.

[0040] The reaction can be carried out in a solvent such as a hydrocarbon, ether or ketone, and an excess of epichlorohydrin can be used as a solvent.

[0041] In epoxy resin of Formula 1 in which 20~100% of X is glycidyl group, the content of the glycidyl group can be appropriately adjusted depending on various factors such as the amount of epichlorohydrin used, reaction temperature, reaction pressure, reaction time, and types and amount of catalysts used.

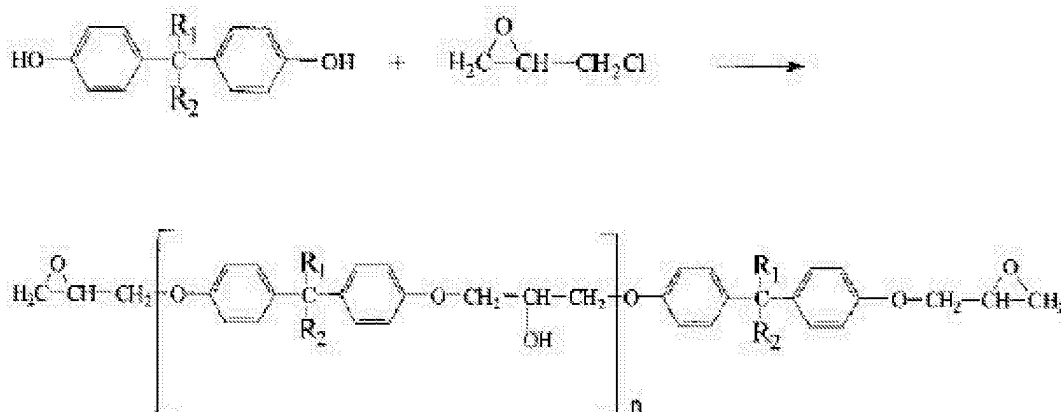
[0042] The multifunctional epoxy resin of the Formula 1 obtained in above reaction has an epoxy equivalent weight of 200 to 600 and an n value of 1 to 30.

[0043] The epichlorohydrin of the Formula 3 is preferably added in an excess amount relative to the bisphenol-A epoxy resin of the Formula 2. The molar ratio of the bisphenol-A epoxy to the epichlorohydrin is 1:30 to 1:80.

[0044] The bisphenol-A epoxy resin of the Formula 2 has preferably an epoxy equivalent weight of 400 to 2000, and more preferably an epoxy equivalent weight of 400 to 1000.

[0045] The bisphenol-A epoxy resin of the Formula 2 can be selected among products commercially available, without being particularly limited. The bisphenol-A epoxy resin of the Formula 2 can also be prepared according to Equation 2 below.

Equation 2



wherein R_1 , R_2 and n are as defined in the Formula 1.

[0046] As shown in the Equation 2, the conventional bisphenol-A and the epichlorohydrin of the Formula 3 can react to form the bisphenol-A epoxy resin of the Formula 2.

EXAMPLES

[0047] The invention will be described with reference to, but is not limited to, the following examples.

Reference Example 1 : Preparation of multifunctional epoxy resin

[0048] 65 parts by weight of bisphenol-A epoxy resin (epoxy equivalent weight 650, $n = 3.4$), 46.3 parts by weight of epichlorohydrin and 0.2 parts by weight of tetramethylammonium chloride were charged into a flask equipped with a reflux apparatus, a stirring apparatus, a vacuum apparatus and a dropping apparatus. 48%(w/w) aqueous solution of 8.5 parts by weight of sodium hydroxide was added to the dropping apparatus. While the aqueous sodium hydroxide solution was added dropwise to the flask under reflux at 50~60°C and 80 torr (10665.76 Pa) over 2 hours, water was removed by azeotropic distillation. After the mixture was further reacted for 2 hours, it was cooled and filtered. Solvents were removed by an evaporator to prepare a desired multifunctional epoxy resin (epoxy equivalent weight 340, G [the ratio of glycidyl group in X of Formula 1] = 65% (EP-1)).

Reference Example 2 : Preparation of multifunctional epoxy resin

[0049] 47.5 parts by weight of bisphenol-A epoxy resin ∇ (epoxy equivalent weight 475, $n = 2.1$), 46.3 parts by weight of epichlorohydrin and 0.2 parts by weight of tetramethylammonium chloride were charged into a flask equipped with a reflux apparatus, a stirring apparatus, a vacuum apparatus and a dropping apparatus. 48%(w/w) aqueous solution of 5.5 parts by weight of sodium hydroxide was added to the dropping apparatus. While the aqueous sodium hydroxide solution was added dropwise to the flask under reflux at 50~60°C and 80 torr (10665.76 Pa) over 2 hours, water was removed by azeotropic distillation. After the mixture was further reacted for 2 hours, it was cooled and filtered. Solvents were removed by an evaporator to prepare a desired multifunctional epoxy resin (epoxy equivalent weight 310, $G = 62\%$) (EP-2).

Reference Example 3 : Preparation of multifunctional epoxy resin

[0050] 200 parts by weight of bisphenol-A epoxy resin \angle (epoxy equivalent weight 1000, $n = 5.8$), 46.3 parts by weight of epichlorohydrin and 0.2 parts by weight of tetramethylammonium chloride were charged into a flask equipped with a reflux apparatus, a stirring apparatus, a vacuum apparatus and a dropping apparatus. 48%(w/w) aqueous solution of 15 parts by weight of sodium hydroxide was added to the dropping apparatus. While the aqueous sodium hydroxide solution was added dropwise to the flask under reflux at 50~60°C and 80 torr (10665.76 Pa) over 2 hours, water was removed by azeotropic distillation. After the mixture was further reacted for 2 hours, it was cooled and filtered. Solvents were removed by an evaporator to prepare a desired multifunctional epoxy resin (epoxy equivalent weight 420, $G = 55\%$) (EP-3).

Reference Example 4 : Preparation of multifunctional epoxy resin

[0051] 47.5 parts by weight of bisphenol-A epoxy resin ∇ , 92.5 parts by weight of epichlorohydrin and 0.4 parts by weight of tetramethylammonium chloride were charged into a flask equipped with a reflux apparatus, a stirring apparatus, a vacuum apparatus and a dropping apparatus. 48%(w/w) aqueous solution of 4.9 parts by weight of sodium hydroxide was added to the dropping apparatus. While the aqueous sodium hydroxide solution was added dropwise to the flask under reflux at 50~60°C and 80 torr (10665.76 Pa) over 2 hours, water was removed by azeotropic distillation. After the mixture was further reacted for 2 hours, it was cooled and filtered. Solvents were removed by an evaporator to prepare a desired multifunctional epoxy resin (epoxy equivalent weight 278, $G = 82\%$) (EP-4).

Reference Example 5 : Preparation of multifunctional epoxy resin

[0052] 65 parts by weight of bisphenol-A epoxy resin \in , 162 parts by weight of epichlorohydrin and 81.0 parts by weight of dimethyl sulfoxide were charged into a flask equipped with a reflux apparatus, a stirring apparatus, a vacuum apparatus and a dropping apparatus, and then 9.1 parts by weight of sodium hydroxide was slowly added thereto at 70°C with stirring. After the addition, the reaction mixture was further reacted for 3 hours. Unreacted epichlorohydrin and dimethyl sulfoxide were removed under reduced pressure. The reaction product containing byproduct salts and dimethyl sulfoxide was dissolved in 150 parts by weight of methylisobutyl ketone, and then 2 parts by weight of 30% aqueous sodium hydroxide solution was added thereto. After the mixture was further reacted at 70°C for 2 hours, it was cooled and oil/water-separated. Solvents were removed by an evaporator to prepare a desired multifunctional epoxy resin (epoxy equivalent weight: 295, $G = 90\%$) (EP-5).

Reference Example 6 : Preparation of multifunctional epoxy resin

[0053] 100 parts by weight of bisphenol-F epoxy resin ∇ (epoxy equivalent weight 1000, $n = 6.6$), 46.3 parts by weight of epichlorohydrin and 0.4 parts by weight of tetramethylammonium chloride were charged into a flask equipped with a reflux apparatus, a stirring apparatus, a vacuum apparatus and a dropping apparatus. 48%(w/w) aqueous solution of 4.9 parts by weight of sodium hydroxide was added to the dropping apparatus. While the aqueous sodium hydroxide solution was added dropwise to the flask under reflux at 50~60°C and 80 torr (10665.76 Pa) over 2 hours, water was removed by azeotropic distillation. After the mixture was further reacted for 2 hours, it was cooled and filtered. Solvents were removed by an evaporator to prepare a desired multifunctional epoxy resin (epoxy equivalent weight 320, $G = 65\%$) (EP-6).

Reference Example 7 : Preparation of multifunctional epoxy resin

[0054] 50 parts by weight of bisphenol-A epoxy resin \textcircled{R} (epoxy equivalent weight 700, $n = 3.7$), 130 parts by weight

EP 1 323 759 A1

of epichlorohydrin and 0.4 parts by weight of tetramethylammonium chloride were charged into a flask equipped with a reflux apparatus, a stirring apparatus, a vacuum apparatus and a dropping apparatus. 48%(w/w) aqueous solution of 8.5 parts by weight of sodium hydroxide was added to the dropping apparatus. While the aqueous sodium hydroxide solution was added dropwise to the flask under reflux at 50~60°C and 80 torr (10665.76 Pa) over 2 hours, water was removed by azeotropic distillation. After the mixture was further reacted for 2 hours, it was cooled and filtered. Solvents were removed by an evaporator to prepare a desired multifunctional epoxy resin (epoxy equivalent weight 304.5, G = 85%) (EP-7).

Examples 1 to 12 : Preparation of powder coating composition

[0055] After each multifunctional epoxy resin prepared in Reference Examples 1 to 7 and components shown in Table 1 were mixed, each mixture was passed through the extruder ZSK25 (W&P, Main screw rpm: 250). The extruded mixtures were ground and applied onto the surface of metal using a GEMA electrostatic spray gun (60-80KV). The metal was cured at 140°C.

Comparative example : Preparation of powder coating composition

[0056] A powder coating composition having the composition shown in Table 1 below was prepared in the same manner as described in the Example 1.

Table 1

Components	Examples												Comp. Example
	1	2	3	4	5	6	7	8	9	10	11	12	
Multifunctional epoxy resin (EP-1)	90	69											
Multifunctional epoxy resin (EP-2)			65										
Multifunctional epoxy resin (EP-3)				78									
Multifunctional epoxy resin (EP-4)					77	59							
Multifunctional epoxy resin (EP-5)							81	57					
Multifunctional epoxy resin (EP-6)									83				
Multifunctional epoxy resin (EP-7)													
Bisphenol-A epoxy resin of Formula 4		29	28	33		32		38	35	95	64	49	
KD-242G											43	67	140
KP-3520	210	202	207	188	223	210	219	206	182	205	193	184	160
Benzoin	5	5	5	5	5	5	5	5	5	5	5	5	5
PV5	5	5	5	5	5	5	5	5	5	5	5	5	5
BaSO ₄	50	50	50	50	50	50	50	50	50	50	50	50	50
TiO ₂	150	150	150	150	150	150	150	150	150	150	150	150	150
2-methylimidazole	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

[0057] All numeral values in Table 1 are expressed as part by weight.

[0058] In the composition of the Table 1, the trademark KD-242G (made by KUKDO CHEMICAL Co., LTD) is a universal bisphenol-A epoxy resin for powder coating compositions with an epoxy equivalent weight of 650-725 g/eq, and the trademark KP-3520 (made by KUKDO CHEMICAL Co., LTD) is a polyester resin for a powder coating composition as a curing agent.

[0059] The benzoin and the trademark PV5 (made by Wolee) were used as a defoaming agent and a leveling agent, respectively. The BaSO₄ as a filler, the TiO₂ as a pigment, and the 2-methyl imidazole as a curing promoter were used.

[0060] Experiment : Impact test, Erichsen test and gellation time measurement.

[0061] Impact test, Erichsen test and gellation time measurement were conducted for the examples 1-12 and comparative example. The results are shown in Table 2 below. The methods for the tests are as follows.

[0062] The Impact test was conducted according to ASTM D2794.

[0063] The Erichsen test was conducted according to ISO1520.

Table 2
Results of impact test and Erichsen test

Tests		Example												Comp. Example
		1	2	3	4	5	6	7	8	9	10	11	12	
Impact strength (Direct, 1kg/50cm)	130°C×20 min.	O	O	O	O	O	O	O	O	O	Δ	O	O	X
	140°C×15 min.	O	O	O	O	O	O	O	O	O	O	O	O	X
	150°C×10 min.	O	O	O	O	O	O	O	O	O	O	O	O	X
Erichsen (8mm)	130°C×20 min.	O	O	O	O	O	O	O	O	O	O	O	O	X
	140°C×15 min.	O	O	O	O	O	O	O	O	O	O	O	O	X
	150°C×10 min.	O	O	O	O	O	O	O	O	O	O	O	O	X
Gellation Time (Sec.)	130°C	170	225	235	250	160	185	150	180	220	147	168	230	421
	140°C	104	130	140	150	100	105	98	105	123	95	104	138	275
	150°C	65	80	83	85	62	67	60	67	78	57	65	82	183

O : good, Δ: slight crack, X : crack

[0064] As can be seen from the Table 2, the results of the impact test and Erichsen test show that the examples 1-12, which comprise the multifunctional epoxy resin of the present invention, are excellent in mechanical properties, compared with the comparative example, under the same curing condition.

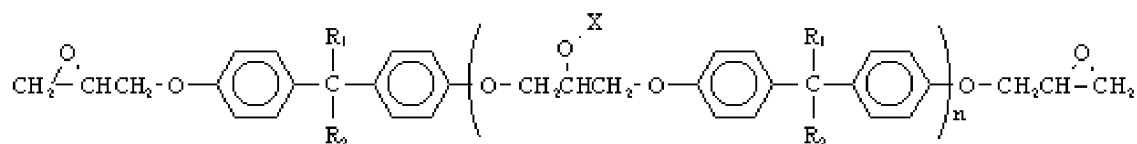
[0065] As apparent from the above description, the powder coating composition comprising the multifunctional and low temperature curable epoxy resin of the present invention has excellent curability at a low temperature, thereby capable of being applied to thick metallic coating objects that cannot reach an elevated temperature within a short time, or coating objects that are thermally sensitive. Accordingly, the present invention is advantageous in terms of energy savings and environmental protection, because sufficient curing can be accomplished with a small amount of energy.

Claims

1. A powder coating composition, comprising:

- 100 parts by weight of a low temperature curable epoxy resin, represented by Formula 1 below:

Formula 1

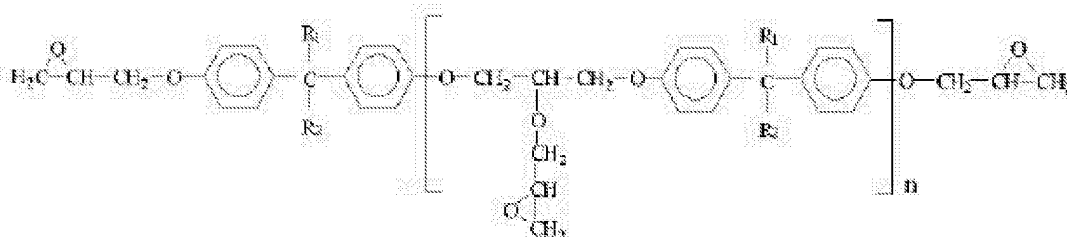


wherein :

- n is a real number of from 0.1 to 30 ;
- R₁ and R₂ are, independently, a hydrogen, or an unsubstituted or substituted alkyl or alkoxy group having from 1 to 5 carbon atoms ; and
- X is a hydrogen atom or a glycidyl group, wherein more than 20% of X are glycidyl groups; and
- 30 to 500 parts by weight of a curing agent.

2. The powder coating composition as set forth in claim 1, wherein the epoxy resin is represented by Formula 4 below:

Formula 4



wherein R₁, R₂ and n are as described in claim 1.

3. The powder coating composition as set forth in anyone of claims 1 and 2, wherein R₁ and R₂ are all methyl, and n is a real number of 1 to 15.

4. The powder coating composition as set forth in anyone of claims 1 to 3, which comprises 0.1 to 20 parts by weight of a defoaming agent and 0.1 to 20 parts by weight of a leveling agent.

5. The powder coating composition as set forth in anyone of claims 1 to 4, wherein the curing agent is a phenolic

curing agent or a polyester-based curing agent.

- 5 6. The powder coating composition as set forth in anyone of claims 1 to 5, which comprises 10 to 200 parts by weight of a universal bisphenol-A epoxy resin for powder coatings having an epoxy equivalent weight of 600 to 1500g/eq, based on 100 parts by weight of the low temperature curable epoxy resin represented by Formula 1.
- 10 7. The powder coating composition as set forth in anyone of claims 1 to 6, which further comprises at least one additive selected from the group consisting of a pigment, an antioxidant, a filler, a light stabilizer, a curing promoter and an ultraviolet absorber.

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EUROPEAN SEARCH REPORT

Application Number
EP 02 10 2833

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EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 10 2833

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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